

Visualizing pigment distributions and their degradation products in oil paintings using a non-destructive macroscopic XRF/XRPD scanning system

F. Vanmeert^a, W. De Nolf^a, G. Van der Snickt^a, S. Legrand^a, J. Dik^b, and K. Janssens^a

^aAXES, Department of Chemistry, University of Antwerp, Belgium

^bMAA, Department of Materials Science, Delft University of Technology, The Netherlands

Author Email: frederik.vanmeert@uantwerpen.be

Over the past years macroscopic X-ray fluorescence (MA-XRF) has proven to be a useful tool for imaging of large cultural heritage objects, e.g. oil paintings.^[1-3] The resulting elemental maps provide complementary information to methods such as X-ray radiography (XRR) and Infra-red reflectography (IRR) that are traditionally used for the investigation of these artworks, and can be used to study the distribution of various pigments on or beneath the surface. However, a main limitation of MA-XRF is that the distribution images are element-specific rather than pigment-specific. This becomes a problem for example when the pigments lead white (cerussite, PbCO_3 and/or hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), red lead (minium, Pb_3O_4), Naples Yellow (bindheimite, $\text{PbSb}_2\text{O}_6 \cdot \text{PbO}$ or rosiaite, PbSb_2O_6) and Lead Tin Yellow (Pb_2SnO_4) are used together, which will all contribute to the Pb-L and Pb-M distribution maps. A second drawback of this technique is the energy-dependent sampling depth for the different elements. The elemental images corresponding to low energy X-rays such as e.g. Pb-M, K-K, Ca-K show information limited to only the top surface of the painting, while for lighter elements such as, e.g. Na, Si, P no fluorescence signals are detected.

To overcome the above-mentioned limitations, a laboratory macroscopic X-ray powder diffraction (MA-XRPD) system has been constructed employing a monochromatic ($\text{Ag-K}\alpha$) X-ray source of low angular divergence ($\text{I}\mu\text{S}^{\text{HB}}$, Incoatec), delivering about 10^7 ph/s in a focal spot of around 100 μm and a single photon-counting X-ray diffraction camera (PILATUS 200K, Dectris). This system allows for the simultaneous recording of XRF and XRPD distribution images from macroscopic objects with a typical lateral resolution in the 0.1 – 1 mm range and dwell times per pixel of several seconds (1-10 s).

Both in our laboratory as well as on-site, a series of measurements on oil paintings from various artists and time periods were performed that reveal meaningful pigment-specific distribution images of different crystalline compounds such as lazurite ($\text{Na}_4\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$), azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), calcite (CaCO_3), hydrocerussite, cerussite, cinnabar (HgS), bindheimite, etc. yielding information on both visible and covered paint layers. Furthermore, the results highlight the different usages by the artists of cerussite and hydrocerussite, both of which are found to be present in different compositions in the pigment lead white. As a final part the presence of various compounds that are believed to have formed over time as alteration products on these artworks will be discussed.

References

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